ULTRAVIOLET ABSORPTION SPECTRA OF DIPHENYL IN THE LIQUID AND SOLID STATES*

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ABSTRACT. The ultraviolet absorption spectra of thin films of diphenyl of different thicknesses in the liquid state at 80°C and solid state at 30°C and -180°C have been investigated. It has been observed that the very broad band lying in the region 2900 Å 2300 Å in the spectrum due to the liquid is split up into two broad bands at 36306 and 37386 cm^{-1} in the case of the solid at 30°C. There are also indications of broad feeble bands up to about 2850 Å. When the solid is cooled to -180°C these feeble bands become sharper and are clearly resolved into nine distinct narrow bands and each of the two broad intense bands observed in the case of the solid at 30°C, splits up into four components at the low temperature. The significance of these results has been discussed It has been pointed out that these new feeble bands of the solid at -180°C may be due to transitions in one of the phenyl rings with the second one in the excited state

INTRODUCTION

Recent investigations on the absorption spectra of some organic compounds in the liquid and solid states at different temperatures including that of liquid oxygen (Deb, 1951*a*, 1951*b*, 1952; Swamy, 1951, 1952*a*, 1952*b*) yielded interesting results. It was found by comparing the results with those for the vapour that the bands shift to longer wavelengths when the vapour is liquefied and they shift some times towards shorter and some times towards longer wavelengths with freezing of the liquid and cooling down to −180°C. Splitting up and sharpening of bands, change of vibrational frequency, etc. were observed in some cases on cooling the substances to −180°C. The compounds studied in the recent investigations were mainly substituted benzene compounds. It was further observed that the changes taking place in the spectrum at low temperatures are different in the case of different substituents. The general similarity in the changes in the spectra, namely the disappearance in the liquid state of the fine structures of bands of vapour state and their partial reappearance at low temperatures is also not observed in some cases, for examples, in the methyl and ethyl benzoates, where the number of bands is the same in liquid and solid states at low temperatures and also the bands do not become appreciably sharp at −180°C.

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In the present investigation the absorption spectrum of diphenyl at different temperatures have been studied in order to find out whether the presence of a phenyl group as a substituent produces any remarkable changes in the electronic energy levels of the molecule.

London (1945) has calculated the energy levels of diphenyl molecule from consideration of the perturbation of the original energy levels of of benzene caused by the presence of the second benzene ring. According to him, four electronic transitions to the ground state are possible at about 2400 Å, 1900 Å, 1500 Å, and 1400 Å. The experimental results in the region about 2400 Å by Seshan (1936) and by Becke [unpublished work, reported by London, (1945)] have been compared and discussed in the present investigation.

EXPERIMENTAL

The experimental arrangement used was the same as that used by the author previously (Deb, 1951a). Chemically pure diphenyl obtained from Merck's original packing, was redistilled in evacuated double bulbs. A very thin film of the substance was necessary to produce bands and this was was obtained by the method described earlier. It was found that the thickness of the absorbing film which produced bands distincitly in the region 2970 Å-2800 Å at low temperatures gave complete absorption for regions of shorter wavelengths. When the thicknesses was still further reduced it was possible to get bands in the region from 2800 Å to 2640 Å, beyond which again there was complete absorption. No bands could be observed at wavelengths below 2640 Å even when the thickness of the substance was reduced still further, though slight absorption was found upto about 2200 Å, the limit of the spectrograph. Films of different thickness were used in the case of the liquid as well as in the case of the soild at different temperatures.

Spectrograms were taken on Ilford Q 1 plates using an Adam Hilger E 1 quartz spectrograph which has a dispersion of about 4 A.U. per mm in the region of 2800 Å. The exposure time was 8 minutes in the case of the liquid state and solid state at room temperature and 30 minutes for the solid at $-180°C$. Iron arc comparison spectrum was taken in each photograph. A hydrogen discharge tube, run at about 3 K.V. was the source of the ultraviolet continuum Microphotometric records of the spectra were taken using a self-recording microphotometer supplied by Kipp and Zonen. The frequencies of the bands were measured from these records in which the record of a known iron line at one end of the spectrum was taken as a reference line and the wavelengths were calculated from the known values of the enlargement (1.6 : 1) and the distances of the peaks from the iron line mentioned above.

RESULTS AND DISCUSSION

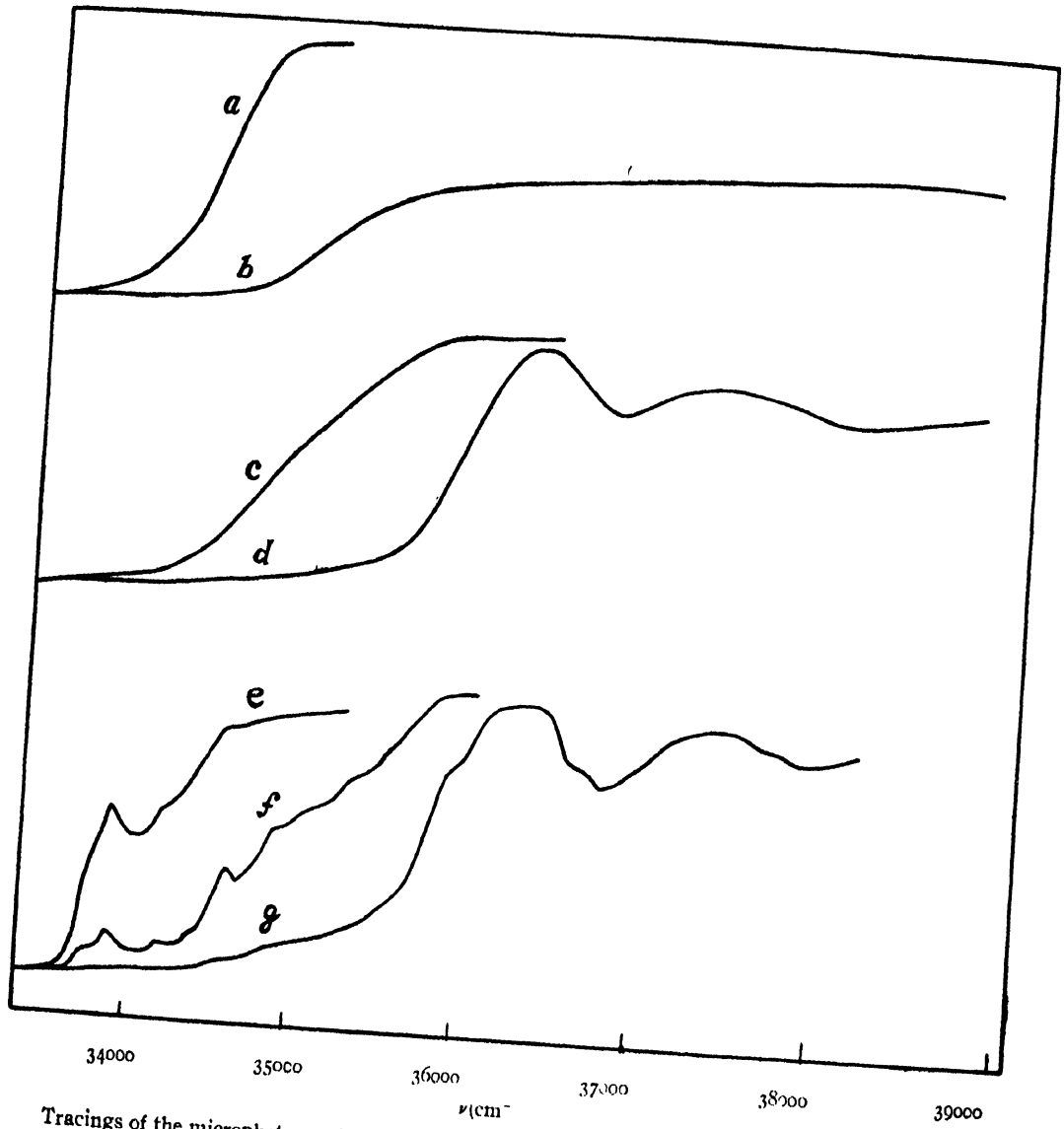
The tracings of the microphiptometric records of the spectra are reproduced in figure 1, and the wave numbers of bands and their assignments are given in Table I.

TABLE I

Ultraviolet absorption bands of diphenyl

Liquid at 80°C	Solid at 30°C		Solid at 180°C		
	ν (cm^{-1})	Assignment	Band no. and Int.	ν (cm^{-1})	Assignment
Continuous absorption commencing at about 2900 Å.	Very feeble broads absorption humps just preceptible.		1 (m)	33751	ν_0
			2 (s)	33911	ν_0+160
			3 (w)	34210	ν_0+468
			4 (vw)	34460	ν_0+709
			5 (s)	34627	$\nu_0+709+160$
			6 (s)	34803	ν_0+1142
			7 (w)	35052	ν_0+1301
					$\nu_0+1142+160$
			8 (w)	35250	$\nu_0+1142+468$
			9 (vw)	35608	$\nu_0+1142+709$
One structureless band between 2850Å-2300Å (with smaller thickness of the absorbing film).	36306		1 (s)	35938	ν_0 (A_0)
			2 (vs)	36101	ν_0+266 (B_0)
	37386	ν_0+1080	3 (vs)	36465	ν_0+537 (C_0)
			4 (ms)	36740	ν_0+812 (D_0)
			5 (w)	37012	ν_0+1084 (A_1)
			6 (ms)	37274	$\nu_0+1084+266$ (B_1)
			7 (w)	37554	$\nu_0+1084+537$ (C_1)
			8 (w)	37824	$\nu_0+1048+812$ (D_1)

As pointed out by previous workers (Seshan, 1936, London 1045) the absorption spectrum of diphenyl in the vapour state gives uniform absorption without any structure over the wide region between 2800 Å and 2200 Å, although the bands due to benzene and most of the substituted benzenes lying in this region have definite structures. The substance, however, shows absorption having banded structures (Carr and Stücklen, 1936) for other systems below 2000 Å, which is beyond the range of the quartz spectrograph. On liquefaction, no change in the absorption spectrum is observed but with the increase in thickness of the film, the region at which absorption begins shifts to about 2900 Å (figure 1, curves *a* and *b*). The solid at 30°C yields a spectrum quite different from that due to the liquid. The single broad absorption band splits up into two broad bands with centres at 36306 and 37386 cm^{-1} (figure 1, curve *d*) respectively. The spectrum due to larger thickness of the absorber reveals the presence of very broad low absorption



Tracings of the microphotometric records of the absorption spectra of diphenyl

Curves (*a*, *b*) Liquid at 80°C

,, (*c*, *d*) Solid at 30°C

,, (*e*, *f*, *g*) Solid at −180°C

Curves (*a*), (*c*), (*e*) and (*f*) were obtained with absorbing films of nearly same thickness, and curves (*b*), (*d*) and (*g*) with a much thinner absorbing film.

humps between 2900 Å and 2750 Å (figure 1, curve *c*). These humps are resolved as sharp absorption peaks when the temperature of the solid film is reduced to −180°C (curve *f*) and the spectrum further undergoes remarkable changes. Each of the two broad bands observed at the room temperature is found to be split up into four components thus giving rise to several progressions (curve *g*). The wavenumber difference between the first components of the two bands is found to be 1084, which is equal to that

between the centres of the unresolved bands observed for the crystal at 30°C. The new absorption peaks lying between 2900 Å and 2750 Å increase in height with the increase of the thickness of the absorbing film at −180°C (curve *e*).

The analysis of the bands thus obtained offers considerable difficulty if all the bands from 2963 Å are supposed to belong to the same system. The degrees of absorption at the new bands also suggest that these may belong to an entirely new system. Probably in the liquid state the feeble bands are also so broad that they merge into one another. Angular oscillations and translational motion of the molecules may be responsible for the for the width. In the case of the fairly thick film at 30°C the bands lying between 2900 Å and 2750 Å can be just identified but they are still very broad.

Angular oscillations persisting in the solid may be responsible for this large width of bands. The solid film at −180°C yields sharp bands in the region mentioned above probably owing to cessation of the angular oscillation of the molecules. These feeble bands have been assumed to belong to the first system and the bands at 36306 and 37386 cm^{-1} form the second system in the case of the solid at 30°C. The weak system due to the crystal at 30°C cannot be analysed owing to the large width of the individual bands. In the case of the crystal at −180°C the first band of this system at 33751 cm^{-1} has been taken as the 0, 0 band of the first system. On this assumption progressions of frequencies 160, 468, 709 and 1142 cm^{-1} have been observed in this system.

In the case of the second system the difference in frequencies of the two bands due to the crystal at 30°C is 1084 cm^{-1}. Each of these two bands is observed to be split into four bands when the crystal is cooled to −180°C. Two alternative explanations can be suggested for this phenomenon. The difference between frequencies of successive components is about 266 cm^{-1}. Hence it can be assumed that this splitting of the bands is not due to the fact that the four components represent vibrational frequencies which are resolved only at −180°C owing to the decrease in their width at the low temperature, but the splitting is due to the splitting of the energy levels by the intermolecular field in the crystal at −180°C Alternatively it can be assumed that the frequency differences 266, 537, 812 and 1084 cm^{-1} represent four vibrational frequencies of the excited state. In the case of this system only one of the phenyl rings is excited, the other being in the ground state. In the diphenyl molecule two carbon atoms of the two benzene rings are joined by C—C bond and the first feeble system may be due to energy levels of one of the rings when the second one is in the excited state. The difference in the excited state vibational frequencies observed in the case of the two systems may also be due to the fact that the frequencies of vibration while both the rings of the molecule are in excited states are lower than those for the first ring with the second one in the ground state. The transi-

tion to the excited state of one of the rings when the other ring is at the excited state may lower the energy difference and this may be the reason why the feeble bands lie on the long wavelength side of the strong bands at 36306 and 37386 cm^{-1} respectively. The probability of such transitions is very low and this explains the low intensity of the bands on the long wavelength side.

The centre of the group of components in each of the two bands in the second system seems to be slightly on the shorter wavelength side of the corresponding bands observed in the case of the solid at 30°C. The bands thus shift towards shorter wavelengths with lowering of temperature of the crystal. Such a phenomenon has been observed in the case of many substituted benzenes (Swamy, 1952, 1953). The splitting of the broad bands at low temperatures may be due to formation of virtual bonds between neighbouring molecules in the crystal.

Investigations with other substances are in progress.

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